COLORIMETRIC DETERMINATION OF ACETYLENE AND ITS APPLICATION TO THE DETERMINATION OF WATER

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CONTENTS

INTRODUCTION

In the course of the examination of certain carefully purified organic compounds it was found that a simple, quick, and very delicate qualitative test for water, showing approximately the amount present, can be made in the following manner: The substance under examination is placed in contact with calcium carbide in the presence of a solvent for acetylene, and any acetylene formed by the action of water is detected by adding the resultant solution to an ammoniacal solution of cuprous chloride. When alcohol or acetone is used as the solvent for acetylene a clear colloidal solution of an intense-red color is formed. Since this reaction appeared to present possibilities as a direct colorimetric method for the determination of water, an effort was made to apply it for this purpose. The results first obtained were very discordant, and it soon became apparent that a careful examination of all the factors which could affect the result would be necessary before any satisfactory procedure could be devised. The investigation of these factors has resulted in the development of a quick and very sensitive method for the determination of acetylene. The application of this method to the determination of water, especially the determination of very small amounts of water in materials of high purity, which was the primary object of the investigation, has been much less successful. The principal sources of difficulty and error in this determination are pointed out in the section of the paper dealing with the determination of water (p. 54). The simpler qualitative methods which are also described (p. 56) have been found very satisfactory, however.

The development of the method for the determination of acetylene will be described in Part I. All of the work upon the detection and determination of water has been brought together in Part II, although much of this work preceded the development of the colorimetric method for the determination of the gas itself.

Part I.—THE DETERMINATION OF ACETYLENE

A. LITERATURE

The use of an ammoniacal solution of a cuprous salt for the determination of acetylene appears to have been introduced by Berthelot.[1] The reagent was greatly improved for qualitative work and its preparation much simplified by Ilosvay,[2] who prepared solutions of cuprous salts by reducing the corresponding cupric salts with hydroxylamine. Ilosvay's investigation was confined to the preparation of the most sensitive qualitative reagent possible. The formation of a red colloid when a small amount of cuprous chloride is added to a solution of acetylene in water was observed by Kuspert,[3] but no attempt to use the reaction for analytical purposes appears to have been made by him or others.

Before proceeding to make experiments upon a colorimetric method for determining acetylene it was necessary to determine the amount of acetylene used in such experiments by an independent procedure, and Berthelot's method of precipitating copper carbide and determining the copper in the precipitate was chosen. An examination of the papers which have been published describing the method for making this determination, together with those relating to the composition and properties of copper carbide, leaves some doubt as to the precautions which must be taken to insure accuracy. The principal point concerning which there appears to be disagreement is the effect of oxidation upon the composition of the precipitated copper carbide. When freshly precipitated in a reducing solution this compound dissolves readily, and, as shown by Scheiber and Reckleben,[4] completely in hydrochloric acid; but if exposed to the air for any considerable length of time before the addition of hydrochloric acid, a black insoluble residue, a product of partial oxidation of either acetylene or copper carbide, is left behind. If this carbonaceous residue is formed directly from acetylene, or if its formation from copper carbide is accompanied by the formation of soluble copper salts, it is obvious that the results obtained in the determination of acetylene will be too low when it is present. The difficulty of

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[1] Compt. rend., 54, p. 1070; 1862.

[2] Ber., 32, p. 697; 1899.

[3] Z. anorg. Chem., 34, pp. 453-454; 1903.

[4] Ber., 44, p. 221; 1911.

preventing this oxidation is shown by the fact that Keiser's[5] efforts to prepare copper carbide free from this substance were unsuccessful and that several other experimenters seem to have had a similar experience. Keiser regarded the residue as carbon; Scheiber[6] determined its composition as $C_{11}H_8O_2$. While the exact composition of the residue has little significance in connection with the determination of acetylene, its method of formation is important.

It might be inferred from the experiments of Keiser and those of Soderbaum[7] that at least a part of the residue is formed by the incomplete oxidation of acetylene; in this case, of course, part of the acetylene would be used up and the amount of copper carbide formed would be less than corresponds to the amount of acetylene absorbed. However, Scheiber's determinations of the composition of copper-carbide precipitates containing a considerable amount of insoluble matter showed, within narrow limits, a constant molecular ratio of copper to carbon of 1 : 1. If the insoluble portion was formed directly by the oxidation of acetylene and the remainder of the acetylene had formed Cu_2C_2, the carbon would certainly have been in excess.

If, on the other hand, the large amount of carbonaceous residue sometimes observed is produced by the oxidation of the copper compound, one of two conditions must exist: (1) Either the copper must form some other insoluble compound, in which case the oxidation would not affect the subsequent determination of the copper, or (2) a corresponding amount of soluble copper salts would be formed, which would be removed in washing the precipitate, leading to serious error. Blochman[8] describes copper carbide as being unstable in the air, and Scheiber[9] found that it increases in weight when dried in the air. Erdmann and Makowka[10] state that the washed precipitate may be exposed to the air on a filter for two or three hours and then washed with dilute acetic acid without a trace of copper being dissolved, but if the exposure to the air is continued long enough the following reaction takes place:

$$2\,Cu_2C_2 + H_2O + 4\,O = (CH_3COO)_2Cu + 3CuO$$

[5] Am. Chem. J., **14**, p. 285; 1892.
[6] Ber., **41**, p. 3816; 1908.
[7] Ber., **30**, p. 762; 1897.
[8] Ber., **7**, p. 74; 1874.
[9] Z. anal. Ch., **48**, p. 537; 1909.
[10] Z. anal. Ch., **46**, p. 129; 1907.

These authors state that copper carbide is less subject than copper sulphide to oxidation by the air.

In their work on the formation of diacetylenyl Noyes and Tucker [11] found that copper carbide will rapidly reduce a solution of cupric chloride, the probable reaction being indicated by the following equation:

$$2Cu_2C_2 + 2CuCl_2 = C_4Cu_2 + 2Cu_2Cl_2$$

Practically all of the observers of the properties of copper carbide, except Blochmann, who found the compound easily changed in air, seem to have worked with a precipitate produced by the complete precipitation of copper by an excess of acetylene. This was certainly the case in the experiments of Erdmann and Makowka. Keiser found that copper carbide has a strong tendency to occlude substances in solution. If acetylene is occluded in this manner, this fact, together with the reaction of Noyes and Tucker, would fully explain Erdmann and Makowka's observation that no copper is made soluble by a brief exposure to the air, since the copper salts would, at first, be reprecipitated by the occluded acetylene as fast as formed by oxidation. When, however, the precipitate is formed in the presence of an excess of a cuprous salt, the formation of cupric salts would be expected to take place immediately on exposure to the air.

B. PRELIMINARY EXPERIMENTS

1. SOLUBILITY AND OXIDATION OF COPPER CARBIDE

Since the literature on the subject does not make entirely clear the effect of oxidation on the determination of acetylene by this method, it seemed advisable to make a few preliminary experiments before using the method for the determination of acetylene in the standard solutions.

The complete insolubility of copper carbide noted by all observers was first confirmed by precipitating, with an excess of acetylene, a copper-sulphate solution which had been reduced by hydroxylamine. The precipitate was filtered and washed freely with dilute ammonia and with water. No trace of copper could be detected by the use of hydrogen sulphide in either the filtrate or the washings.

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[11] Am Chem. J., **19**, p. 123; 1897.

In another experiment a limited amount of acetylene was passed into a cuprous-chloride solution containing hydroxylamine. The precipitate was filtered and then washed with water containing a little ammonia and hydroxylamine without allowing air to come in contact with the precipitate. About 200 cc of wash water was required before the washings showed no trace of copper by the ferrocyanide test. After this the precipitate was further washed with 50 cc of dilute ammonia and then with 50 cc of water in order to remove hydroxylamine. The precipitate was then covered with 50 cc of dilute ammonia of the strength used for washing and air was bubbled through the liquid, portions being drawn off through the filter from time to time and tested for copper. Potassium ferrocyanide gave a positive test for copper almost immediately and in the course of about 15 minutes the liquid was colored distinctly blue by dissolved cupric-ammonium salts. Finally, the liquid was drawn off and the precipitate exposed to the air overnight. When water was added a large amount of cupric salt went into solution at once.

This experiment made it evident that in order to obtain accurate results in the determination of acetylene by the cuprous-chloride method it would be necessary to exclude air during the whole procedure.

In the hope of avoiding the difficulty of excluding air, experiments were made with silver salts as a substitute for cuprous chloride. It was found that the silver in silver carbide can be readily and accurately determined; but the reaction of acetylene with ammoniacal solutions of silver nitrate was found to be so slow that the use of this method was impracticable. The experiments made on this point confirm the conclusions of Rivett.[12]

2. COMPOSITION OF SOLUTION FOR PRECIPITATING COPPER CARBIDE

The experiments with silver nitrate having proven solutions of that salt to be unsuitable for the determination of acetylene, cuprous chloride was used. An absorption apparatus[13] was employed which permitted the filtration and washing of the precipitate without exposure to the air. The inclined tube in which absorption took place was about 60 cm long and the gas bubbles remained in contact with the liquid 8 to 10 seconds.

[12] Chem. News, **104**, p. 261; 1911.

[13] See Fig. 2 in the article by Weaver and Edwards, J. Ind. Eng. Chem., **7**, p. 534; 1915.

A series of experiments of a qualitative nature was made to determine the composition of the absorbing solution which would give the best results. The comparative rates at which hydrogen containing acetylene could be passed through different solutions in the apparatus without showing a trace of acetylene in a second apparatus was one of the tests used; but the most useful criterion of the speed of absorption was the distribution of the precipitate which adhered to the glass in the absorption tube. When using the best absorbing solution practically all of the acetylene was precipitated within 20 cm of the inlet, and the glass beyond that point remained free from precipitate. When absorbing solutions were used which permitted the escape of some of the acetylene into the second wash bottle the precipitate was distributed throughout the length of the absorption tube. The absorbing solutions tested in this way contained varying amounts of cuprous chloride, ammonia, ammonium chloride, and hydroxylamine.

The solution which was found to give the best results was made by adding 1 g of cuprous chloride, 1 g of hydroxylamine hydrochloride, and 10 cc of concentrated ammonium hydroxide to 50 cc of water. When the gas was passed through this solution at a moderate rate no trace of acetylene could be detected at the outlet of the absorption apparatus by passing the gas through more of the same solution. After filtering and washing, the precipitates of copper carbide dissolved completely and rapidly in dilute hydrochloric acid. The amount of acetylene was calculated from the amount of copper present in this solution as determined by one of the usual methods.

3. CHOICE OF A PROTECTIVE COLLOID

In order to keep the copper carbide in the colloidal form and to prevent precipitation with a resultant change of color, it is necessary to add a protective colloid. Gelatine, dextrine, gum arabic, and water glass were tried for this purpose. The gelatine solutions were invariably found to be the most uniform and permanent, confirming the results of Küspert.[14] Consequently, gelatine was used in the preparation of all the solutions used in subsequent work.

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[14] Z. Anorg. Chem., 34, p. 453–454; 1903.

4. CHOICE OF A PRELIMINARY COLOR STANDARD

A primary requirement for a colorimetric method is a standard for comparison. Obviously, the most satisfactory standard for use with a colored solution is a solution of the same character having a known value, provided such a standard is sufficiently permanent or readily reproducible; a colloidal solution of copper carbide possesses neither of these requirements. When sealed in a glass tube a solution of the colloid containing a considerable excess of hydroxylamine has been kept for as much as a week without apparent change; but a solution in a sealed tube is not a convenient standard for comparison in a colorimeter. Even though oxygen is wholly excluded, the deep blue color of cupric-ammonium salts will eventually appear in consequence of the reaction $Cu_2Cl_2 = CuCl_2 + Cu$, which takes place quite rapidly in ammoniacal solution. It is also very difficult, if not altogether impossible, to make a sufficiently accurate standard by the use of known amounts of acetylene or of water, since the small amounts required could be measured with sufficient accuracy only in very dilute solution, and dilute solutions of either are very hard to keep without change.

It would be useless to describe in detail the many unsuccessful efforts that were made to obtain a suitable standard. Colloidal solutions of copper ferrocyanide and of copper carbide made by passing an excess of acetylene into dilute solutions of cuprous salts were found unsuitable. After trying a very large number of organic dyes a solution having the following composition was chosen as the most suitable and convenient standard:

Chromanilbraun R	milligram	0.21
Carmoisine B	do	.04
Gum arabic	grams	2.5
Water	cubic centimeters	100.00

This solution was designated on an arbitrary color scale as standard "H 25" and will, for the sake of brevity, be so designated in this paper. Unless the contrary is stated it may be assumed that this solution was used in all the observations which follow. Further experiments with color standards and their evaluation will be described in a later section of this paper (p. 45).

C. DEVELOPMENT OF COLORIMETRIC METHOD

1. APPARATUS AND METHOD EMPLOYED

(a) APPARATUS

A solution of acetylene in ether, measured from an ordinary burette, was used as the source of acetylene. The use of such a solution seemed especially desirable, since it eliminated the variables affecting the amount of acetylene evolved from a constant weight of water when reacting with calcium carbide; and at the same time permitted an exact duplication of the conditions which appeared to be most favorable for the quantitative evolution and determination of acetylene from small amounts of water, i. e., solution in ether with subsequent distillation, in a stream of hydrogen, into the absorbing solution. The results would therefore be applicable in the investigation of the water method itself.

The apparatus used for the purpose is illustrated in Fig. 1. The standard solution of acetylene in ether was contained in the bottle *A* connected, through a siphon, with the lower end of burette *C*. The air drawn into either the burette or bottle to replace the solution used was passed through the wash bottle *B* containing some of the same solution. The stoppers and connecting tubes were sealed in place with paraffin to form air-tight connections.

The acetylene solution was measured from the burette *C* into the flask *D*. The funnel *P* served for the introduction of ether which did not contain acetylene. A stream of hydrogen from the Kipp generator *G* carried the acetylene and ether vapor over into the absorbing solution contained in *E*. *E* was graduated to facilitate the preparation and measurement of the absorbing solution. When the ether in *D* was completely evaporated, the colloidal solution found in *E* was run into the colorimeter tube *F* and compared with the standard contained in another tube not shown in the figure. The depth of solution in the colorimeter was read in the side tube *J*, which was backed by a millimeter scale. The gas outlet tube from *E* was connected with *J* in order that a stream of hydrogen might be used to sweep the bulk of the air out of *F* and thus assist in preventing the oxidation of the cuprous

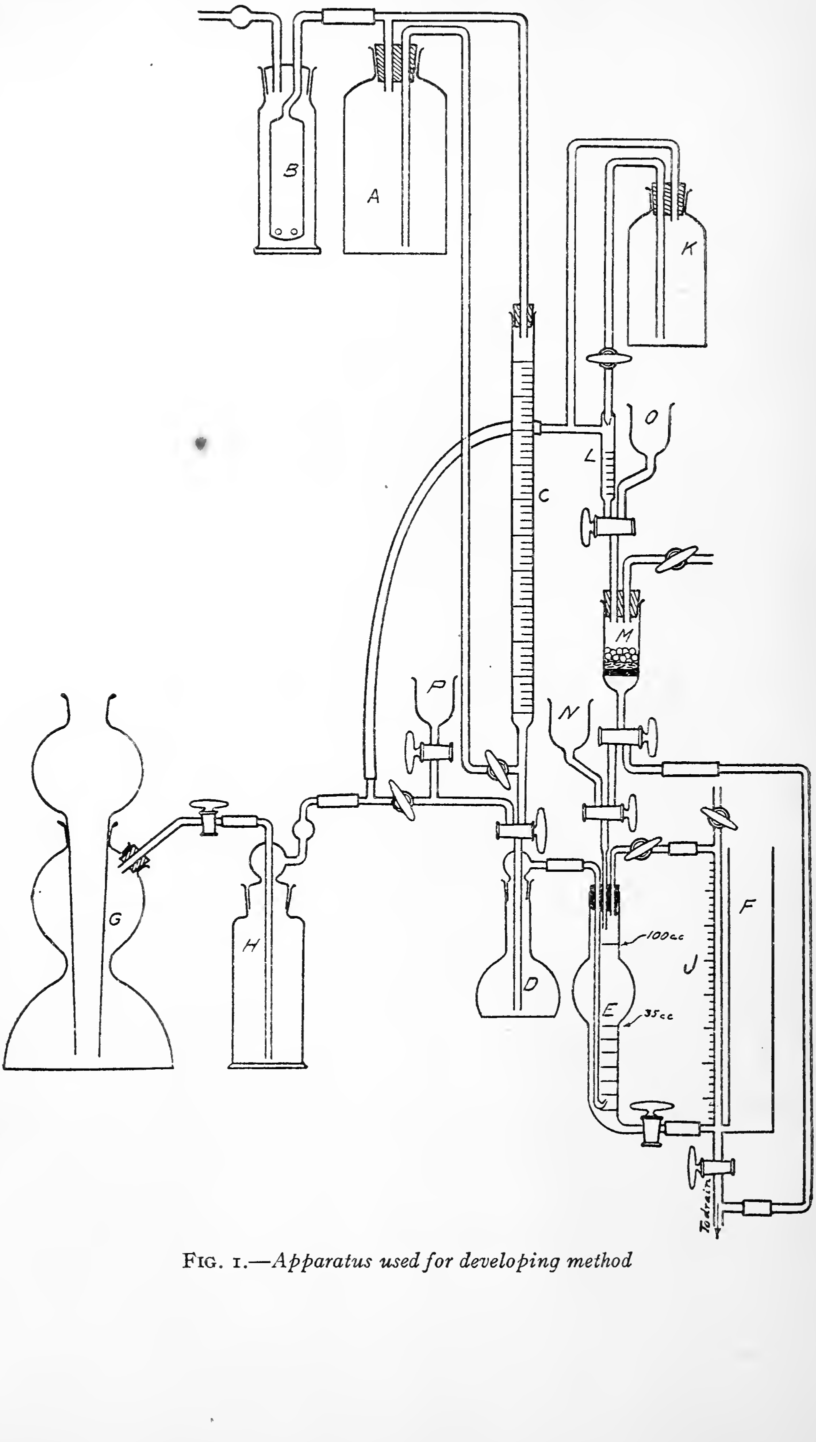

FIG. 1.—*Apparatus used for developing method*

chloride in the colloidal solution. This precaution was found to be unnecessary for any ordinary work, but the arrangement proved very useful when making a large number of comparisons with a single colloidal solution, as in the work with standards described on page 46.

The wash bottle *H* was partially filled, during many of the experiments, with an alkaline solution of pyrogallol to remove any considerable amount of oxygen or acid gases present in the hydrogen used. It served at all times to indicate the rate at which hydrogen was passing and to detect leaks in the connections.

The bottle *K*, containing a hydrochloric-acid solution of cuprous chloride, was protected from access of air by connecting to the hydrogen supply. The solution of cuprous chloride was measured in the graduated tube *L* and run into water contained in *M* which caused the cuprous chloride to precipitate. *M* contained a filter of asbestos resting on a perforated porcelain plate and held in place by a layer of glass beads. The cuprous chloride was filtered and washed, the operation being facilitated by pressure from *G*. After filtration and washing the cuprous chloride in *M* was dissolved through the filter with ammonium hydroxide and run into *E*. The other constituents of the absorbing solution were added through the funnel *N*.

Since an ammoniacal solution of cuprous chloride can not be preserved, owing to the formation of cupric salts with the separation of copper, it was found most convenient to keep the cuprous chloride in hydrochloric-acid solution and to precipitate and wash the salt just before use.

The colorimeter used was of simple construction, resembling that described by Campbell and Hurley.[15] The light from a tungsten lamp was diffused by an opal glass, and reflected from a second opal glass through the comparison tubes to a pair of mirrors set at an angle of 45°. The light is reflected from these mirrors to the eye, producing a divided field.

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[15] J. Am. Chem. Soc., **33**, pp. 1112–1115; 1911.

(b) PREPARATION OF STANDARD ACETYLENE SOLUTION

The standard solution of acetylene in ether was prepared by passing into 500 cc of ether for several minutes a stream of acetylene which had been generated from specially prepared calcium carbide and washed with water. The calcium carbide used was prepared for this purpose by Dr. C. W. Kanolt of this Bureau from pure precipitated calcium carbonate and a considerable excess of sugar charcoal, and was entirely free from sulphur and phosphorus. The acetylene produced had a pleasant odor and produced a pure white precipitate in an ammoniacal solution of a silver salt. The strong acetylene solution thus prepared was diluted with ether to obtain an acetylene concentration convenient for use.

The acetylene in the standard solution was determined from time to time by attaching the absorption apparatus used for the experiment upon the gravimetric method to the outlet of the evolution flask (*D*, Fig. 1), running 10 cc or more of the standard acetylene solution from the burette into the evolution flask, and passing a stream of hydrogen through the apparatus until the ether was entirely evaporated and the apparatus completely swept out with hydrogen. The precipitate was filtered, washed with water containing a small amount of ammonia and hydroxylamine hydrochloride, and dissolved with dilute hydrochloric acid. The copper in the solution was then determined by one of the following well-known methods:

1. The solution was evaporated to dryness and the copper chloride converted to acetate and determined by the iodometric method.

2. The copper was precipitated from hydrochloric-acid solution as sulphide, ignited, and weighed as copper oxide.

3. The chloride was converted to sulphate and the copper determined electrolytically.

Table 1 shows the agreement obtained between duplicate determinations of the acetylene in solution at different times. Many single determinations not shown in the table were made at other times.

TABLE 1

Determination of Acetylene in Standard Solution

Solution used	Date	Volume of solution used	Method for copper	Copper found	C_2H_2 per cubic centimeter of solution
		cc		mg	mg
A	Mar. 15	10	Iodometric	25.5	0.522
		10	.....do	25.8	.528
B	Mar. 27	16	Sulphide	24.7	.315
		10	.....do	15.5	.317
		10	Iodometric	15.4	.315
B	Apr. 18	10	Sulphide	9.8	.200
		10	.....do	10.0	.204
		10	.....do	9.9	.202
B	June 11	10	Electrolytic	5.0	.102
		10	.....do	4.9	.100
		10	Sulphide	5.1	.104
C	July 30	10	Electrolytic	7.8	.159
		10	.....do	7.8	.159

2. FACTORS AFFECTING COMPLETENESS OF ABSORPTION AND COLOR OF COLLOID

(*a*) METHODS OF STUDY

The influence of the variable factors affecting the formation of the colloidal solution was investigated by absorbing definite amounts of acetylene, from measured volumes of the standard solution, in 30 cc of absorbing solution. After the absorption was completed this solution was diluted to 100 cc before comparing with the color standard in the colorimeter.

The values used for determining the absolute amount of acetylene taken in each experiment were calculated from the results of the last analysis of the standard solution made before and the first analysis made after the experiment in question, on the assumption that the change in concentration of the acetylene solution was uniform during the period. This assumption was certainly not exactly correct, since it was found that the rate of change of the acetylene solution was largely dependent upon temperature changes in the laboratory. However, since it was

the purpose of these experiments only to show the effect of a single variable at a time, it was only necessary that the results of each series should be comparable with one another. For this reason the observations of any one series were all made between 9 a. m. and 11 p. m. of a single day, with the exception of one series, which were conducted within a continuous period of 32 hours. In no case was the change in strength of the acetylene solution, during the period covered by a series of tests, sufficient to be detected by the colorimeter.

In each comparison the depth of solution in one tube remained constant while the depth of solution in the second tube was varied until the two appeared to match. This comparison was repeated several times, or as often as necessary to fix the depth of solution required in the second tube within 1 mm.

The results obtained in the 65 tests which were first made, under conditions not subsequently found to cause serious error, were plotted, and a curve was drawn to approximate the average of these results.

Values taken from this curve (called acetylene found) were used to compare the relative amounts of acetylene which would be indicated by tests made under the various conditions. Since only relative values were required, it was not necessary to know the exact position and slope of the curve which would give absolute values. The exact form of the curve fixed by the final series of determinations, made after the effects of all variables had been investigated, is shown in Fig. 5.

(*b*) RESULTS OBTAINED

(1) Size of Tip and Rate of Gas Flow.—During many of the earlier tests hydrogen carrying acetylene was introduced through a glass tip about 2 mm in diameter. It was evident that absorption was not complete when using this tip, since a ring of red precipitate always formed on the glass at the upper surface of the absorbing liquid. Tests made by passing the gas into a second portion of the absorbing solution always showed the presence of acetylene when any large amount was present in the original sample. A tube with a fine tip about 0.2 mm in diameter, curved

so that bubbles escaping from the tip would pass through the solution without coming in contact with the glass after leaving the tip, was substituted. All subsequent experiments indicated that the absorption of acetylene from the very fine bubbles produced by the use of this tip was practically complete. At the most only a faint trace of red precipitate appeared on the glass at the surface of the solution after several runs, and no color whatever was produced in a second absorption apparatus.

Comparisons of the results obtained by the use of the two tips indicated that, at the rate of flow used for the previous comparisons (about 35 cc of hydrogen per minute), about 30 per cent of the ascetylene had escaped. When the rate of gas flow was increased to 75 cc per minute, while still using the 2 mm tip, the loss of acetylene amounted to more than 50 per cent. When the 0.2 mm tip was substituted, it was found that the results were independent of the rate of gas flow at rates of 5 to 50 cc per minute. Even at a rate of 100 cc per minute the loss amounted to only about 10 per cent.

(2) Composition of Absorbing Solution.—Tests were made to determine the influence of the following constituents in the solution used for absorption: Cupric chloride, ammonium chloride, hydroxylamine hydrochloride, cuprous chloride, ammonia, gelatin, alcohol, and acetone.

The data obtained from the many tests do not, in general, lend themselves to convenient tabulation and plotting, hence only the conclusions drawn from the tests are given here.

In the following discussion of results the amount of each of the various constituents mentioned as present in the solution is always the amount contained in 30 cc.

Cupric Chloride.—It was found that the presence of even quite large amounts of cupric chloride in the absorbing solution is without appreciable effect, provided a sufficient amount of the cuprous salt is also present during the absorption and enough hydroxylamine is added before the colorimetric comparison to reduce all cupric salts. Cupric chloride may be added to a colloidal solution already prepared and left for several hours without affecting the colloid, as shown by colorimetric tests after reducing the cupric

salts with hydroxylamine. If the solution is exposed to the air the colloid is unaffected until the cuprous salts in solution are oxidized; then the colloid quickly disappears with the formation of a flocculent black precipitate.

Ammonium Chloride.—The presence of ammonium chloride, or, indeed, any strong electrolyte, causes irregular and generally low results. Ten milligrams of the salt in 30 cc of absorbing solution produced a tendency toward low results. Twenty milligrams caused results averaging 40 per cent low and more than that amount caused precipitation. The presence of ammonium chloride in the absorbing solution is the most serious single source of error in the colorimetric determination of acetylene. After its effect was discovered, solutions showing the characteristic brownish and slightly turbid appearance caused by the presence of much of the salt were discarded.

Hydroxylamine Hydrochloride.—The presence of a small amount of hydroxylamine hydrochloride in excess of that required to decolorize the absorbing solution is without appreciable effect, but a large excess has the same effect as a small amount of ammonium chloride, e. g., 100 mg of hydroxylamine hydrochloride caused average results about 10 per cent low.

Cuprous Chloride.—Only a very small amount of cuprous chloride is required to give complete absorption of the acetylene and the amount present may be varied over a wide range without affecting the results. Solutions containing from 9 to 360 mg gave identical results. Solutions containing 6 mg gave results about 30 per cent low, although the amount of acetylene was much less than equivalent to the amount of copper, while solutions containing only 3 mg of cuprous chloride gave no color at all.

Ammonia.—The amount of ammonia in solution must be regulated rather carefully. About 10 cc of concentrated ammonium hydroxide (specific gravity 0.90) per 30 cc of solution gives the best results. Irregular results are caused by any considerable change in the concentration in either direction. The use of only 5 cc caused results 40 per cent low while the use of 2.5 cc gave results 60 per cent low. More than 10 cc of strong ammonium hydroxide was likely to produce a cloudy appearance caused by coagulation of the gelatin; 20 cc always caused the formation of a

large amount of precipitate, sometimes enough to leave the solution practically colorless.

Gelatin.—The amount of gelatin may be varied from 2 to 6 mg per 30 cc provided coagulation does not take place. The amount should be kept small to prevent coagulation. Less than 1 and more than 10 mg are almost certain to cause precipitation.

Alcohol.—The presence of a large amount of alcohol favors uniform results, but alcohol causes gelatin to coagulate and the amount which can be used is limited by this fact. About 10 cc of 95 per cent alcohol per 30 cc of solution gave the most favorable results. When only 5 cc was used the results were about 30 per cent low. Less than 5 cc caused precipitation. Too great a variation of the alcohol concentration in either direction causes precipitation.

Acetone.—The effect of substituting acetone for a part or all of the alcohol was tried. In general, the color of the resulting colloid was changed and comparisons with the standard were difficult. Acetone also coagulates gelatin more readily than alcohol.

Preparation of Best Absorbing Solution.—From a consideration of the above results it is easy to determine approximately the most favorable composition for the absorbing solution. The solution which gives the most uniform results is made up as follows: Dissolve 0.25 g of gelatin in hot water, dilute to 500 cc, and add 500 cc of 95 per cent alcohol and 1.25 g of hydroxylamine hydrochloride. To 20 cc of this solution add 10 cc of concentrated ammonium hydroxide and a small amount of cuprous chloride. One or two hundredths of a gram of this salt is all that is required, although as much as half a gram is unobjectionable. If a greater amount of solution is required to fill the absorption apparatus, it should be made up in the same proportions.

(3) TEMPERATURE.—A few experiments on the effect of temperature were carried out in the same manner as those upon the composition of the absorbing solution. The results show that the temperature changes in the ordinary laboratory would not affect the result appreciably. There was a tendency for the results to be low at temperatures above 35° C. Results at 45° to 50° were 10 to 15 per cent low.

(4) RATE OF EVOLUTION OF ACETYLENE.—In order to test the effect of the rate at which the acetylene is evolved—i. e., whether it is added or produced all at once and passed into the absorber rapidly, or whether it is mixed more uniformly with the hydrogen stream—two methods were used: (1) Varying amounts of ether containing no acetylene were introduced into the evolution flask with the fixed amount of the standard solution; this, in effect, is the same as using a more dilute solution with consequent more gradual evolution of the acetylene; (2) the standard solution was introduced in a number of small portions, each of which was nearly or entirely evaporated before adding the next portion, thus more nearly approximating a uniform evolution of acetylene throughout the experiment. The results of these experiments agreed with one another within 0.01 mg of acetylene when using the small tip, showing that no differences greater than the error of observation were caused by the acetylene being evolved at different rates.

(5) VOLUME OF ABSORBING SOLUTION.—The effect of changing the volume of the absorbing solution is shown in Table 2. In each case the composition of the absorbing solution was the same and the solution was diluted to 100 cc before making the colorimetric comparison. Since these experiments were very carefully made after the effect of all variables had been investigated, the tendency to obtain higher results when using the smaller volume of absorbing solution is probably not due to experimental error. It is believed that this effect is due to equilibrium within the solution, the significance of which will appear later.

TABLE 2

Effect of Volume of Absorbing Solution

Volume of absorbing solution, cubic centimeters	Acetylene taken	Acetylene found	Difference
	Mg	Mg	Mg
30	0.68	0.71	+0.03
30	.41	.41	.0
30	.54	.55	+ .01
30	.27	.26	− .01
60	.41	.38	− .03
60	.54	.53	− .01
60	.27	.24	− .03
90	.41	.38	− .03

3. COMPARISON WITH COLOR STANDARD

(a) DILUTION OF SOLUTION AFTER ABSORPTION

A large number of experiments have shown that, within the limit of accuracy of the colorimeter readings, it is immaterial how much the colloidal solution is diluted before the readings are taken, provided the volume of solution is taken into account in calculating the amount of acetylene. For example, if a sample of acetylene is absorbed in 30 cc of solution and the resulting liquid successively diluted with water to 60, 90, and 120 cc and comparisons with the same color standard are made at each dilution, it will be found that the depths of colloidal solution required to match the standard are in the ratios, 1:2:3:4. Some of the results bearing on this point are shown in Fig. 2, and their significance will be pointed out in the discussion of that figure in the following section.

(b) PREPARATION AND STANDARDIZATION OF A COLOR STANDARD

After determining the effect of the various factors influencing the color of the colloidal solutions, it was an easy matter to choose a method of procedure which gives uniform results. When using an absorbing solution of the composition already noted (p. 43) it is only necessary to introduce the gas through a fine tip at such a rate as to insure complete absorption; in the apparatus used, a rate of about 35 cc per minute, controlled by counting the bubbles passing through the wash bottle between the hydrogen generator and the evolution flask, was chosen. In order to determine the amount of acetylene in an unknown gas mixture, however, it was first necessary to prepare and determine more accurately the value of a color standard by comparison with colloidal solutions made from known amounts of acetylene by the chosen method of procedure.

Although it is possible to match very closely any depth of a given colloidal copper-carbide solution with a single dye solution, such as solution "H25," described on page 34, the ratio between the depths of the two solutions is not constant, but varies, with the depth. When comparing small depths, the color—i. e., the relative amount of light of the longer and shorter wave lengths transmitted—is the determining factor in making the comparison.

When a greater depth is used, practically all light except red is excluded and the point of agreement is no longer determined by the color of the two fields in the colorimeter, but by whether one field is lighter or darker than the other.

Numerous comparisons have been made which illustrate these effects. Fig. 2 shows the results obtained by matching different depths and dilutions of two colloidal solutions, *A* and *B*, against standard solution "H25." The figure shows the following points of interest:

1. The variation of the ratio between depths of the colloidal and the standard solutions with change in depth of the standard solution, discussed in the last paragraph, is clearly illustrated. If this ratio were constant, the points would, of course, all lie on a straight line passing through the origin.

2. The degree of accuracy of the colorimeter readings is indicated by the agreement of results between different comparisons with the same solution. When using the standard depth (10 cc) of standard solution, the error of a single comparison should not exceed 5 per cent and the average of several readings should give results much closer.

3. The effect of dilution is noted. At the depth commonly used for comparisons (10 cc of standard solution) the agreement between results on the same solution at successive dilutions of 35, 70, and 100 cc is clearly within the limit of accuracy of the colorimeter readings. At greater depth a divergence is apparent.

4. The agreement between duplicates (solutions *A* and *B* were prepared in the same manner from the same amount of standard acetylene solution) is within the limit of accuracy of the colorimeter readings.

Fig. 3 shows the results of comparisons of different depths of a single colloidal solution made from 0.19 mg of acetylene with four different dye solutions which can be used successfully as standards of comparison. Curve *a* represents the comparisons made with a solution of 1 part of azolitmin in 2500 parts of water; curve *b*, with a solution of 1 part of oxamine red in 50 000 parts of water; curve *c*, with a solution made by acidifying with hydrochloric acid a slightly alkaline solution containing 2 per cent of gum arabic and 1 part in 40 000 of oxamine red; and curve *d*,

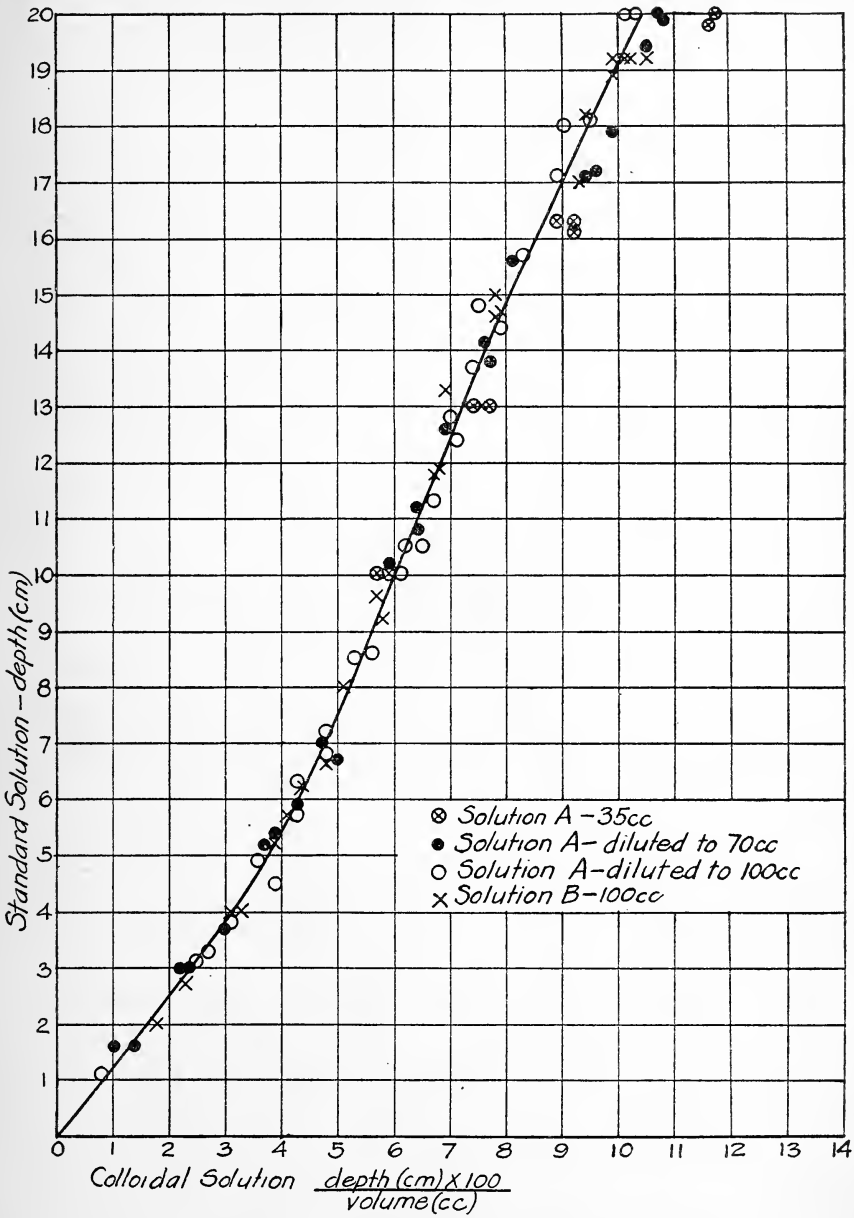

FIG. 2.—*Effect of changing depth of standard solution*

with standard "H25." To avoid confusion, the actual points determined are given for curves *b* and *d* only. The rapid curvature of *a* is due to the fact that azolitmin solutions are almost entirely transparent to red light but screen all other colors even when quite dilute. It will be noted that *d* curves in the direction opposite to the curve in Fig. 2, although made with the same

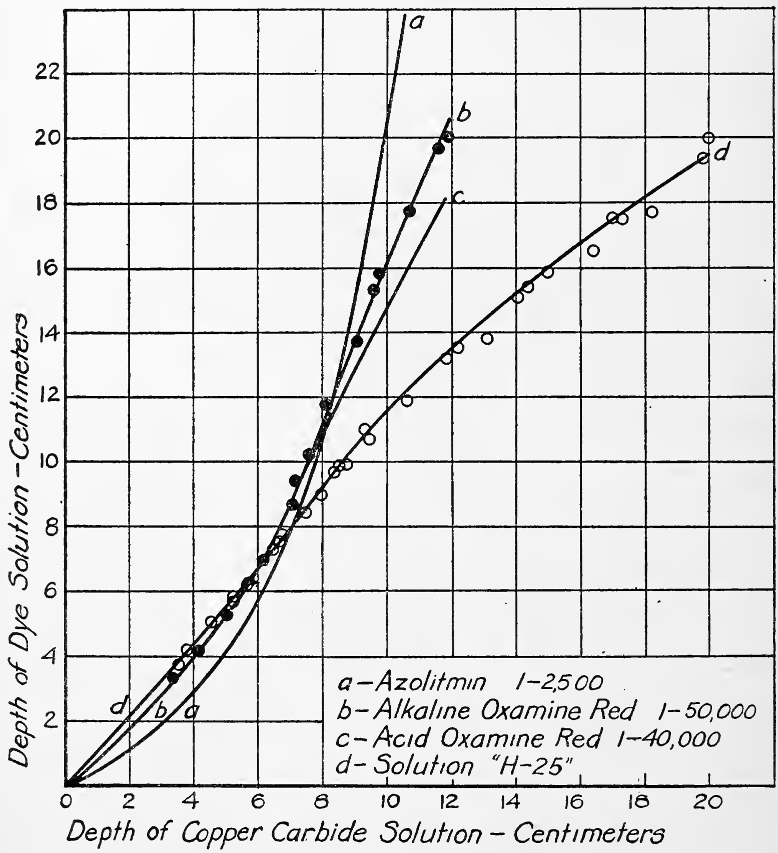

FIG. 3.—*Comparison of color standards*

standard solution. This signifies that the character of the two colloidal solutions was not the same. As compared with the standard, the colloidal solution represented in Fig. 3 was relatively more transparent to red than to blue light. The contrary was true with the colloidal solutions in Fig. 2. This was, no doubt, due to the fact that the colloidal particles were larger in

the latter case than in the former, a condition which may have been caused by the presence of a small amount of ammonium chloride. The transparency to red light decreases rapidly with an increase of the conditions which produce precipitation.

It is evident from a consideration of Figs. 2 and 3 that in order to obtain comparable results it is preferable always to make the comparison of an unknown solution with the same depth of standard solution. In practically all the work described in this paper 10 cm of "solution H25" was used as the standard. When the color of the colloidal solution was so light that the total volume of 100 cc was not sufficient to match 10 cm of the standard (which was the case when prepared from less than about 0.12 mg of acetylene) the whole of the colloidal solution was transferred to the colorimeter and the depth of standard solution varied to match it. The error due to the change in ratio of standard solution to colloidal solution caused by this procedure is always negligible, probably never as much as 0.01 mg of acetylene.

Upon plotting the results of any series of comparisons of the colloidal solutions produced by known amounts of acetylene with a fixed color standard, it appears that within the limits of experimental error the results obtained will all lie on a straight line represented by the equation $x=ay+b$ in which $x=$amount of acetylene, $y=\frac{1}{\text{depth of colloidal solution}}$ and a and b are constants. In this equation b represents, of course, the point at which the curve cuts the horizontal axis, and its value is that of the smallest amount of acetylene which will produce a color in the absorbing solution. The value of a is dependent upon the color standard used. Both constants must be experimentally determined.

When a variable depth of a standard solution is used for the comparison, the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$ may be used as the value for y and the equation $x=ay+b$ still holds, provided the ratio between the depths of the two solutions is the same for all depths. As pointed out in the preceding section, this is not the case with any of the solutions used as standards, but it may be assumed without appreciable error for amounts of acetylene not greater than 0.1 to 0.2 mg. For larger amounts a constant depth

of standard solution should be used in order to provide a color standard of fixed value.

The value of b was, at first, thought to represent the minimum concentration of acetylene in the gas mixture which would be absorbed by the solution. If the existence of such a minimum were the true explanation of the fact that the curve does not pass through the origin, it is evident that a given amount of acetylene diluted with a large volume of hydrogen would give lower results than the same amount of acetylene diluted with a small volume of hydrogen. That such is not the case was shown by the experiments described under the heading "Rate of evolution of acetylene" (p. 44). The only other probable explanation seemed to be that there is an equilibrium in the absorbing solution and that b represents the minimum concentration of dissolved acetylene which will produce a colored colloid. If this is true, the value of b should be proportional to the volume of absorbing solution. The experiments given in Table 3 and plotted in Fig. 4 show that this relation is at least approximately correct.

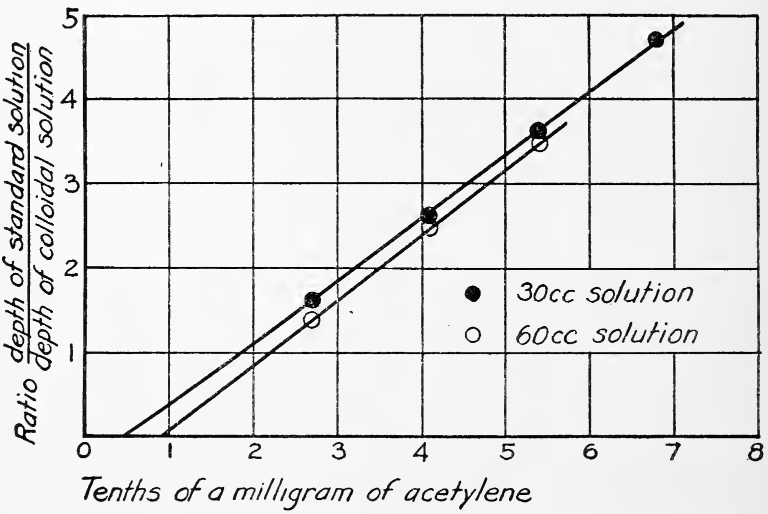

FIG. 4.—*Effect of volume of absorbing solution used*

Fig. 5 shows the results of one series of comparisons of "standard solution H25" with known amounts of acetylene from a carefully analyzed solution in ether. The equation of the straight line averaging these values is $x = 1.43\ y + 0.3$ where x is expressed in

tenths of a milligram of acetylene and y is the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$.

Calibration of any Color Standard.—Since the value of b depends upon the volume of the absorbing solution and is independent of the color standard used, its value may be experimentally fixed once for all. This value has been carefully determined several times under different conditions and has always been found to be between 0.02 and 0.05 mg. It seems probable that in any

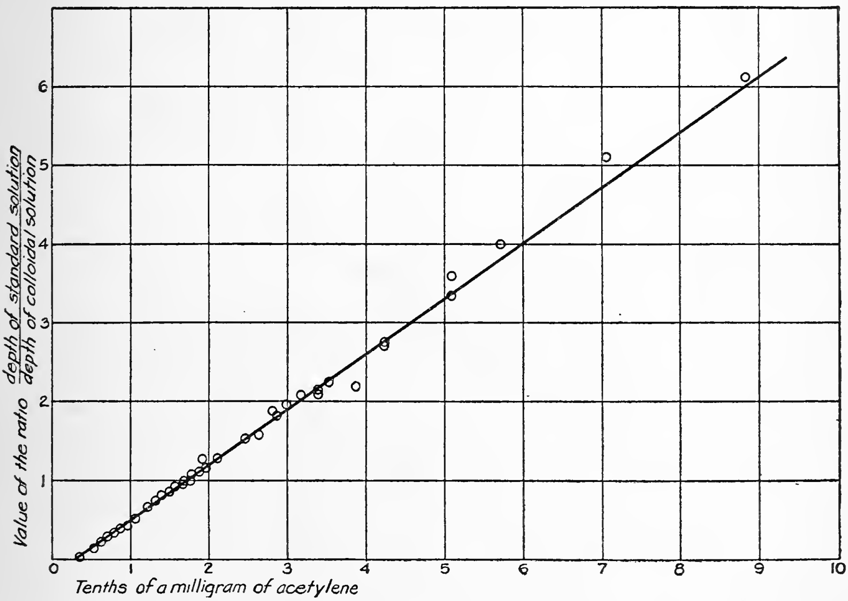

FIG. 5.—*Comparison of standard solution with known amounts of acetylene. Equation of line is $x=1.43y+0.3$*

operations in which there is fairly complete absorption the value of b may be assumed to be 0.03 mg for 30 cc of absorbing solution without causing any error in excess of 0.01 mg. In order to calibrate any color standard it is then only necessary to make one accurate comparison of the standard with a colloidal solution prepared from a known amount of acetylene. This comparison gives simultaneous values for x and y in the equation $x=ay+0.03$, and the value of a may be easily calculated. Unknown amounts of acetylene may then be determined from the same equation,

using the values already found for *a* and *b*, or for convenience a curve may be plotted and values taken from that.

Chemists who desire to make only an approximate determination without the labor of previously calibrating a standard may do so by using as a standard a depth of 10 cm of a solution of 0.04 g of azolitmin in 100 cc of water. The value of *a* for a solution of this strength made from a sample of the dye of Kahlbaum grade was found to be 0.13 mg, *y* representing the ratio between the depth of the two solutions. It is not known how much variation will be found among different samples of azolitmin; but it is apparent from the slope of curve *a* in Fig. 3 that any variation in the strength of the azolitmin solution or the quality of the dye will cause much less than a proportional error in the amount of acetylene found.

As a color standard, a piece of ruby glass or a glass plate covered with a film of gelatin and stained with oxamine red or other suitable dye may be used instead of one of the solutions mentioned on page 46. Once having calibrated the standard as described above, the same results are obtained, no matter what standard is used, provided the two colors are enough alike to permit an accurate comparison and the standard does not change. A ruby glass is, of course, permanent, but the author is unable to say how much reliance may be placed in the permanence of color of a stained film.

Table 3 gives the results of a series of determinations of unknown amounts of acetylene using two different standards for comparison. The results are in substantial agreement.

TABLE 3

Determination of unknown amounts of acetylene, using as standards (1) 10 cm solution H25, a=1.43; (2) ruby glass No. 1, a=3.69

Sample	Acetylene found	
	Solution H25 as standard	Ruby glass as standard
	mg	mg
1	0.51	0.55
2	.43	.41
3	.29	.28
4	.57	.56
5	.56	.55

D. DETERMINATION OF ACETYLENE IN GAS MIXTURES

None of the constituents normally present in illuminating gas interferes in any way with the colorimetric determination of acetylene. To make such a determination it is only necessary to pass a measured volume (0.5 to 2 liters) of the gas into the absorbing solution and make the colorimetric comparison. The whole determination can be made in about 10 minutes. Four successive determinations of the acetylene in illuminating gas taken directly from the house piping gave 0.30, 0.30, 0.32, and 0.33 cc per liter. The method was applied by J. D. Edwards in this laboratory to the testing of hydrogen of high purity. One part of acetylene was readily determined in 250 000 parts of hydrogen from one source. Hydrogen from another source, believed to contain only a small fraction of this amount of acetylene, produced a red stain on the tip of the inlet tube in the absorbing solution, but no coloration in the liquid.

In order to ascertain whether acetylene could be determined in air by this method, a sample of the acetylene solution in ether was first run in the usual manner with a stream of hydrogen to carry it into the absorber; then the determination was repeated, using the same amount of acetylene and a stream of air instead of hydrogen. The acetylene-air mixture was passed through a strongly alkaline solution of pyrogallol and thence into the absorber; and the pyrogallol solution was heated to boiling before the stream of air was stopped. When hydrogen was used the test showed 0.56 mg of acetylene; with air 0.53 mg of acetylene was found. Only one determination was made in air on account of the inconvenience of the apparatus used, but the result showed that acetylene in air can be determined by this method.

The experiment also proved that a solution of potassium hydroxide could be used if necessary to remove hydrogen sulphide, carbon dioxide or similar interfering gases. It was found by several experiments that small amounts of carbon dioxide did not affect the determination, but that larger amounts had the same effect as the introduction of a little ammonium chloride into the solution. The color of the colloid produced by acetylene carried over in a stream of pure carbon dioxide was too brown to admit of any accurate comparison.

Part II.—THE DETECTION OF WATER BY THE USE OF THE ACETYLENE-CUPROUS CHLORIDE REACTION

Calcium carbide has recently been quite extensively used for the determination of water in substances which, for any reason, do not permit the application of the more usual methods of analysis. It was suggested by Berthelot,[16] that the acetylene evolved in the reaction could be determined by absorption in an ammoniacal solution of a silver salt with subsequent titration of the excess of silver. This method was tried by Rivett [17] for the determination of water in butter, but was not successful on account of the incomplete absorption of the evolved acetylene. With this exception, all the chemists who have used the calcium-carbide method seem to have determined the evolved acetylene either volumetrically or by loss in weight. Obviously, neither of these methods is applicable to the detection of very small amounts of water, especially in the presence of other volatile substances.

A. EXPERIMENTS UPON THE QUANTITATIVE DETERMINATION OF WATER

The accurate determination of very small amounts of water by the colorimetric method, which was the primary object of this investigation presents several difficulties which are nearly insurmountable.

Efforts were made to determine water in a variety of materials by the use of the apparatus described below. The sample to be tested was brought into contact with calcium carbide, in a small glass apparatus, either with or without anhydrous ether to act as a solvent. The flask in which the reaction took place was connected to a condenser and thence to a tube filled with carbide to prevent the escape of water vapor. Ether dried over sodium could be introduced directly or could be distilled through a phosphorus pentoxide tube into the reaction flask. The whole apparatus could be swept out with hydrogen dried over phosphorus pentoxide.

[16] Compt. rend., 129, p. 361; 1899.

[17] Chem. News, 104, p. 261; 1911.

The greatest difficulty encountered is due to the fact that calcium carbide itself, or the calcium hydroxide which it always contains, appears to occlude acetylene which it holds with great tenacity but gives off slowly for long periods. It may be that the source of trouble is a small amount of water which is held by the calcium hydroxide and which reacts with the carbide very slowly. Whatever the exact cause, there is no question that with any carbide obtainable commercially all efforts to remove this acetylene by ignition or evacuation have proven unsuccessful. The acetylene which causes the trouble may be removed by boiling the carbide two or three times with an anhydrous liquid such as ether. After such treatment the carbide must not be exposed to the air even for an instant. After the reaction between the carbide and the sample being tested for water is finished, it is necessary to remove the acetylene produced in the same way as before the test. It is apparent that a considerable amount of ether is required for the two purposes and that a large volume of hydrogen is required to sweep out the apparatus completely. It has been found almost impossible to dry ether so thoroughly that the amount required by this test will produce no acetylene which can be detected. Even the ether from a bottle entirely filled with a loose mass of sodium wire, which remains apparently perfectly bright, may produce a surprising amount of acetylene, and phosphorus pentoxide appears to lose very quickly its power to remove the water completely from ether vapor. It is consequently very difficult to secure consistent blanks.

A second source of difficulty, which has been recognized by every chemist who has used the carbide method for the determination of water, is the fact that the calculated amount of acetylene is never produced from a known quantity of water. This is particularly true when dealing with very small amounts of water. In the author's experiments the amount of acetylene produced has varied from 50 to 80 per cent of the calculated amount, generally approaching the latter figure.

In consequence of these sources of difficulty and error, tests made with the colorimeter have little more significance than the much simpler qualitative tests described in the next section. A negative test is quite conclusive, but the detection of an amount

of acetylene less than 0.1 mg has little more than qualitative significance.

Negative tests have shown that the standard samples of benzoic acid, naphthalene, and sugar issued by this Bureau are almost absolutely anhydrous. As an example of the kind of results which may be expected when water is present, the following tests are given of a sample of alcohol in which E. C. McKelvy, of this Bureau, had determined the amount of water by the method of critical solution temperature.[18]

TABLE 4

Determination of Water in Alcohol

By critical solution temperature—A. Water found	By carbide method		Ratio $\frac{B}{A}$
	Acetylene produced	B. Water found	
mg.	mg.	mg.	
1.0	0.48	0.62	0.62
1.0	.58	.80	.80
6.0	3.5	4.8	.80
6.0	3.6	5.0	.82
50.0	[a] 21.2	29.2	.59

[a] Acetylene determined gravimetrically.

B. QUALITATIVE METHOD BY SOLUTION OF ACETYLENE IN AN ANHYDROUS SOLVENT

While the quantitative determination of water by reaction with calcium carbide and distillation of the evolved acetylene into an absorbing solution is a complicated, difficult, and unsatisfactory procedure, the detection of water by permitting the reaction with carbide to take place in the presence of a solvent of acetylene, and adding the acetylene solution formed to a cuprous chloride precipitating solution, is rapid, simple, and accurate. The methods found most satisfactory for carrying out this test will now be described.

1. PREPARATION OF REAGENTS

(a) ANHYDROUS SOLVENTS

When testing for water in organic liquids it is usually most convenient to allow the liquid under test to serve as the solvent for

[18] This Bulletin, 9, p. 344.

acetylene, in which case the previous preparation of an anhydrous solvent is not necessary. In applying the tests to solids, however, it is necessary to allow the reaction with carbide to take place in the presence of an anhydrous liquid, preferably a solvent of the substance under test; and the first difficulty met with in the use of the method was that of preparing even approximately dry solvents. Samples of gasoline, benzene, ether, ethyl acetate, amyl alcohol, amyl acetate, ethyl alcohol, methyl alcohol, acetone, chloroform, carbon tetrachloride, carbon bisulphide, and pyridine were treated with calcium chloride, lime, metallic sodium, metallic calcium, and phosphorus pentoxide, except in those cases where a given drying agent was known to be inapplicable on account of reaction with the solvent. The five solvents first mentioned were thus prepared so nearly free from water that it was impossible to detect a trace of acetylene dissolved in them after several minutes' contact with calcium carbide. Sodium appeared to be the best drying agent for the hydrocarbons and ether, and calcium for the esters. Drying of the other solvents was not carried to completion by the above treatment, but all except pyridine were dried sufficiently to be used successfully as solvents for substances containing any considerable amount of water. The list could, no doubt, be extended almost indefinitely; and nearly all, if not all, of those liquids mentioned could be completely dried by the use of proper drying agents and the observance of suitable precautions. All the liquids tested in this investigation were found to dissolve enough acetylene to give the desired test. Since any of these solvents will, if exposed to the air for a very short time, absorb enough water to show a decisive test, they should be kept, after being dried, in bottles containing some of the drying agent and communicating with the air through a tube containing phosphorus pentoxide. It is difficult to exclude the air sufficiently by the use of ordinary glass, cork, or rubber stoppers unless the pressure differences, due to temperature changes, are eliminated by the use of a drying tube.

The most sensitive tests are obtained when a solvent is employed which is immiscible with water, since the precipitate formed by the subsequent treatment with cuprous-chloride solution, if small in amount, collects at the surface of separation of

the two liquids and is very easily detected. If a fairly large amount of acetylene is present, the aqueous layer dissolves enough acetylene to form a precipitate throughout the solution. When the acetylene is dissolved in liquids miscible with water, such as alcohol and acetone, the copper carbide first appears, of course, in the colloidal form, but unless a protective colloid is present it quickly precipitates. Since the precipitate is distributed through a much larger volume when these solvents are used, the test is not nearly so sensitive as with ether or chloroform with which, as above noted, the precipitate is concentrated in a single layer. Furthermore, with some of the miscible solvents, especially with acetone, the precipitation does not appear to be always complete. In fact, it is sometimes possible to discharge the color of a colloidal solution of copper carbide by adding a large excess of acetone.

(b) PREPARATION OF CUPROUS-CHLORIDE SOLUTION

In case alcohol or acetone is used as a solvent and there is no substance present which will precipitate gelatin, it is probably best to use a reagent which will keep the copper carbide in the colloidal form. The following procedure is recommended:

Make up a solution to contain 0.5 g of gelatin and 2.50 g of hydroxylamine hydrochloride per liter. Take a volume of this solution equal to the volume of alcohol or acetone to be tested for acetylene, add an equal volume of concentrated ammonium hydroxide and a small amount (2 to 10 m per cubic centimeter) of cuprous chloride. As soon as the copper salt is dissolved add the solvent to be tested for acetylene.

The composition of the solution containing the colloid is now the same as that found to be the most favorable for the quantitative determination of acetylene, and the amount of acetylene added in solution may be determined, if desired, by a colorimetric comparison.

When solvents are used which are immiscible with water, or when there are substances present which would precipitate gelatin, the copper carbide must be observed in the form of a precipitate, and the composition of the most suitable reagent is some-

what different. When a colloidal solution is desired it is necessary to use a reagent which will prevent precipitation; when a precipitate is to be observed a reagent must be used which will favor precipitation. Ilosvay[19] made a careful study of the composition of the most sensitive reagent for this purpose; he recommends the following proportions for solutions made from several salts:

1. 0.75 g copper chloride ($CuCl_2.3H_2O$), 1.5 g ammonium chloride, 3 cc ammonium hydroxide (20 to 21 per cent NH_3), 3 g hydroxylamine hydrochloride.
2. 1 g copper nitrate ($Cu(NO_3)_2.5H_2O$), 4 cc ammonium hydroxide, 3 g hydroxylamine hydrochloride.
3. 1 g copper sulfate ($CuSO_4.5H_2O$), 4 cc ammonium hydroxide, 3 g hydroxylamine hydrochloride.

In each case the copper salt is dissolved in a small amount of water, the ammonia and hydroxylamine hydrochloride are added, and the solution is diluted to 50 cc. The first of these solutions seems, in general, to give the most satisfactory results. This solution may be used for the detection of acetylene in any of the solvents previously mentioned except carbon bisulphide, which is reduced to hydrogen sulphide by hydroxylamine and precipitates the copper from the solution as a sulphide. When it is necessary to use carbon bisulphide as a solvent the precipitating solution must be made up from cuprous chloride without the use of any reducing agent. It is very difficult to prepare such a solution which is entirely colorless, but a very small precipitate of copper carbide may be readily detected even in a deep-blue solution, and tests have shown that the presence of a cupric salt does not interfere with precipitation, provided a sufficient amount of the cuprous salt is present.

On account of the difficulty caused by the oxidation of cuprous to cupric chloride, experiments were made with a view to replacing the copper solution with an ammoniacal solution of a silver salt; but the white or yellowish precipitate of silver carbide was so much less characteristic and so much harder to detect in small amounts than the red copper carbide that the formation of the latter is the more useful test even when, as in the presence of carbon bisulphide, the copper solution used can not be decolorized.

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[19] Ber., **32**, p. 697; 1899.

(c) REMOVAL OF ACETYLENE FROM CALCIUM CARBIDE

In order to remove the acetylene (or water) which is always contained in commercial calcium carbide, it is necessary to boil the carbide with one or two portions of the anhydrous solvent, the liquid being completely evaporated before the carbide is used. In case it is not desired to use, for this purpose, the solvent which is subsequently employed in the water determination, anhydrous ether may always be used.

2. METHOD OF MAKING TEST

The test for water is carried out most simply by adding the substance to be tested, together with the solvent, to a few pieces of calcium carbide which have been "boiled out," as described in the preceding paragraph, in a test tube. The test tube is closed by a dry cork or other stopper and shaken occasionally without allowing the liquid to touch the stopper. Two or three minutes' contact with the carbide is usually sufficient. The tube is allowed to stand long enough for the carbide to settle and the clear solvent decanted into the cuprous solution, with which it is vigorously shaken. It might be supposed that small particles of carbide would be carried into the aqueous solution and that the acetylene so produced would make the test of no value; but very little difficulty is experienced from this source. The high density of the carbide causes even very small pieces to settle rapidly, and particles which are carried into the precipitating solution are immediately surrounded by a dense precipitate which causes them to appear as black specks easily distinguished from the bright red, flocculent precipitate produced by dissolved acetylene.

In testing solids, it is preferable to use as a solvent for the acetylene a liquid which also dissolves the solid under examination. This is not absolutely necessary, however, since an anhydrous liquid will generally extract water quite readily from a solid containing it, provided the solid is in a fine state of division. Tests for water in powdered sugar have been made successfully by the use of ether, in which sugar is nearly, if not entirely, insoluble. Tests of nonvolatile acids or other compounds, which it is not desirable to bring into contact with carbide, may be made by adding an anhydrous liquid, which is then distilled off and tested for

water, either by passing over carbide in vapor form or in the usual manner after condensation. Gases may be tested by simply passing over carbide, which has been freed from acetylene, and into the cuprous-chloride solution.

3. BLANK TESTS

Whatever procedure is adopted, it is necessary to make a blank test before using the method to detect water in the sample under examination. When testing an organic liquid by simple contact with carbide and decantation, it is only necessary to insure the removal of all acetylene previously held by the carbide. Boiling out two or three times with the liquid under test or with ether, in the manner already described, is always sufficient to accomplish this. Any acetylene found in portions of the liquid subsequently added is due to water in the sample. When using an anhydrous solvent or when distilling in hydrogen it is necessary to make the blank test in the same manner as the test for water.

4. COMPOUNDS INTERFERING WITH THE TEST

The usefulness of any qualitative test is, of course, largely determined by the number of compounds which will give the reaction in question. Masson [20] states that of all the substances dealt with in ordinary circumstances, water is the only one which has any chemical action on carbide. A consideration of the reaction between water and calcium carbide and that occurring in neutralization shows that in the presence of an acid water might be expected to form as rapidly as it is removed until the hydrogen of the acid has been quantitatively converted into acetylene by the following cycle of reactions:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$
$$Ca(OH)_2 + 2H(A) = Ca(A)_2 + 2H_2O$$

In the case of the weaker organic acids, at least, this does not take place, probably because of the fact that no neutralization occurs in a nearly anhydrous solution, and the formation of acetylene seems to give a good qualitative test for water in spite of the possible reaction between the acid and calcium hydroxide.

[20] Chem. News, 103, pp. 37-38 (1911); J. Chem. Soc., 97, p. 851; 1910.

Masson found that crystalline acids and acid salts, including those which contain water of crystallization readily removed by calcium carbide, do not react as acids, when treated with calcium carbide, with either the carbide or the calcium hydroxide resulting from reaction with the water of crystallization. Experiments by the author with acids in anhydrous solution showed that in some cases, at least, the acid in solution is quite as inactive as were the acids in Masson's experiments. Thus a 1 g sample of fused benzoic acid was dissolved in ether and boiled with calcium carbide under a reflux condenser for 15 minutes without producing a trace of acetylene. Solutions of oleic and phthalic acids have been found to behave in the same manner. Ordinary glacial acetic acid reacts vigorously with the production of acetylene, but neither acetic anhydride, nor acetic acid containing a considerable excess of acetic anhydride, do so. Sulphuric acid of all concentrations, including that containing an excess of sulphur trioxide, causes a continuous slow evolution of acetylene. Even in cases when acetylene is evolved on testing the weaker organic acids, it would, of course, be impossible to say, without first testing acids of known water content, how much, if any, of the acetylene was formed by the acid itself.

In his experiments upon the determination of water by the measurement of the acetylene evolved, McNeil[21] found that a larger volume of gas was evolved from glycerol and from oleic acid than could be accounted for by the amount of water present. In view of the behavior of related compounds, it seemed improbable that this could be due to the production of acetylene from the compounds themselves, except that in the case of oleic acid continuous neutralization and reaction with the water so formed might be expected to take place as with any other acid. In order to test this point, thoroughly dried samples of the two compounds were prepared. The large water content of the best samples available was not materially reduced by heating for three hours at 100°, in a stream of air dried over phosphorus pentoxide and at a pressure of less than half an atmosphere. The oleic acid was therefore dissolved in anhydrous ether, the ether distilled off under reduced pressure, and the acid heated to 110°. This operation was

[21] Bureau of Chemistry, Circular No. 97; 1912.

repeated several times. Glycerol was treated in the same way, using alcohol as a solvent instead of ether. By this procedure, both oleic acid and glycerol were obtained which did not give any trace of acetylene after contact with calcium carbide, either when used alone or in solution in ether or alcohol. An elevated temperature (as high as 120°) did not cause any reaction which could be detected.

5. SENSITIVENESS OF TEST

This method for the detection of water is very sensitive. Numerous tests were made by the simple method of decantation of the solvent after contact with carbide, using samples of gasoline, benzene, and ether, which gave perfect blank tests. Known amounts of water were introduced by adding nearly absolute alcohol, the water content of which had been determined by E. C. McKelvy, of this Bureau, by the method of critical solution temperature.[22]

The results indicated about the same degree of sensibility in the case of the three above-named solvents, 0.01 to 0.03 mg of water per cubic centimeter of the solution in contact with the carbide being the limit at which the formation of a precipitate could be detected. Other tests made by adding a known weight of water dissolved in anhydrous ether showed about the same sensibility. Tests made upon other solvents, in which a blank test showed a trace of water, indicated that the test made with alcohol was less sensitive than with the solvents mentioned above, but more sensitive than with acetone. Ethyl acetate, chloroform and carbon tetrachloride showed about the same sensibility as ether.

SUMMARY

A colorimetric method for the detection of small amounts of acetylene has been developed in the course of an investigation upon the determination of small amounts of water by the use of calcium carbide. The results upon the quantitative determination of water have not been satisfactory, but a simple and very sensitive qualitative test for water is easily made.

The method for the determination of acetylene has been worked out successfully. The determination is made by conducting the

[22] This Bulletin, 9, p. 344.

gas to be investigated into an ammoniacal solution of cuprous chloride containing gelatine and alcohol, and comparing the red colloidal solution so obtained with a suitable standard, which may be either a solution of red dye or a piece of ruby glass.

After a careful investigation of the effect of varying the composition of the absorbing solution the following procedure was adopted in making up the solution: Dissolve 0.25 g of gelatin in hot water, dilute to 500 cc, and add 500 cc of 95 per cent alcohol and 1.25 g of hydroxylamine hydrochloride. To 20 cc of this solution add 10 cc of concentrated ammonium hydroxide and a small amount of cuprous chloride. After the absorption of the acetylene the solution is diluted to 100 cc and compared in a colorimeter with the standard which has been chosen. The standard used in the experimental work was a solution containing chromanilbraun R, carmoisine B, and gum arabic. A more convenient, though less accurate, standard is a fixed depth of a solution of azolitmin. If 10 cm of a solution of azolitmin containing 1 part of the dye to 2500 parts of water is used as standard, the amount of acetylene in 100 cc of colloidal solution may be calculated from the equation $X = 0.13y + 0.03$, where X = number of milligrams of acetylene and $y = 10 \div$ number of centimeters of colloidal solution required to match the standard.

The method is very sensitive. Amounts of acetylene as small as 0.03 mg may be detected and amounts up to 2 mg may be determined with an accuracy of better than 0.05 mg.

Hydrogen sulphide and large amounts of oxygen and carbon dioxide interfere with the test, but all of these may be removed by passing the gas to be tested through a hot alkaline solution of pyrogallol without loss of acetylene.

A qualitative test for water, sensitive to less than 0.1 mg, may be very easily and quickly made by bringing the substance to be tested into contact with calcium carbide in the presence of a solvent for acetylene, which is then decanted or distilled into an ammoniacal solution of cuprous chloride. Nearly all the common organic liquids are suitable for use if carefully dried. The method is applicable to a great variety of substances and especially to volatile organic compounds. The only compounds known to interfere with the test are the stronger acids and substances, such

as hydrogen sulphide, which precipitate cuprous salts from solution.

The investigation required some experiments upon the determination of larger amounts of acetylene by precipitation with cuprous chloride and subsequent determination of the copper. It was found that in order to obtain accurate results by this method it is absolutely necessary to carry out the filtration and washing of the precipitate in the absence of air.

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